

### REMARKS

The Office Action of December 6, 2005 presents the examination of claims 36, 39 and 41-52. Claims 39 and 41-52 are allowed.

The sole issue precluding allowance of the present application is a rejection of claim 36 under 35 U.S.C. § 103(a) as being unpatentable over Sato JP '977, Pohl '233, Williams et al. '080 and Beratan '063, for the reasons of record. This rejection is respectfully traversed. Reconsideration and withdrawal thereof are requested.

The Examiner cites Sato as describing that a photochromic film can be made by steps of grafting of a viologen onto a polymeric substrate via pendant benzyl chloride groups, coating that layer with a "donor such as polyaniline". The Examiner cites Williams for the steps of forming the viologen by reaction of the pendant benzyl chloride with 4-4' bipyridiyl and an organic dihalide. Beratan is cited for the proposition that polyaniline is a well-known electron donor.

Applicants once again submit that the cited references fail to establish *prima facie* obviousness of the claimed invention. In particular, there is no teaching or suggestion by the combined references that a conductive polymer can be obtained by irradiation of polyaniline-coated viologen. This feature of the invention is totally lacking from the combined teachings of the references.

The Examiner again states that "[P]hotoreduction of a a viologen salt by polyaniline occurs by electron transfer when irradiated ...due to electroconductivity...". (Emphasis in original.) This statement highlights the Examiner's misunderstanding of the invention. Electron transfer is the mechanism of an oxidation-reduction reaction. Electron transfer does **not** imply conduction, *i.e.* movement of electrons through a material under the influence of a voltage gradient.

As yet further evidence of this distinction, Applicants provide attached papers by Kamogawa et al. and by Sampanthar et al.

Kamogawa et al. show the exchange of an electron between a viologen molecule and a halide ion. See, e.g. the reaction scheme below Figure 2 on page 1022. The negatively charged halide ion is converted to a neutral halogen atom, and the positively charged tertiary amine of the viologen is also rendered neutral, with the result that the viologen absorption spectrum changes and the viologen becomes colored. This is a classic example of an oxidation-reduction reaction and also of photochromism as described by Sato. Sampanthar et al. show essentially the same reaction in the instance of viologen grafted to a LDPE substrate.

The Examiner should note that all of Sato, Kamogawa and Sampanthar suggest that the electrons transferred remain localized. There is no suggestion whatsoever that any material is formed that would provide for electron flow under an imposed voltage gradient, i.e. that an conductive material would be made.

The Examiner also has not yet responded to Applicants assertion that she has mischaracterized the teachings of the Beratan reference. In their previous response, Applicants explained that:

The Examiner states that Beratan discloses that polyaniline is a suitable electron donor for a viologen salt acceptor. Beratan does not make any conductive material comprising polyaniline. Beratan shows redox cycling between aniline and viologen monomer units in a polymer using a ruthenium bipyridine intermediate. See, col. 6, lines 18-22. Such a composition is far afield from one comprising a viologen salt and polyaniline as distinct substances.

Thus, Beratan in fact describes a material that is a co-polymer of aniline and viologen, not an article comprising polyaniline and viologen. Accordingly, the combined references in fact make no suggestion of irradiation of an article comprising polyaniline and viologen to obtain a conductive material.

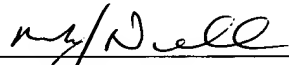
For at least the reasons explained above, the combination of Sato JP '977, Pohl '233, Williams et al. '080 and Beratan '063 fail to expressly describe or to suggest the subject matter of claim 36. Accordingly, the standing rejection of claim 36 under 35 U.S.C. § 103(a) over these references is improper and should be withdrawn.

The present application well-describes and claims patentable subject matter. The favorable action of allowance of the pending claims and passage of the application to issue is respectfully requested.

Should there be any outstanding matters that need to be resolved in the present application, the Examiner is respectfully requested to contact Mark J. Nuell (Reg. No. 36,623) at the telephone number of the undersigned below, to conduct an interview in an effort to expedite prosecution in connection with the present application.

Dated: March 3, 2006

Respectfully submitted,

By 

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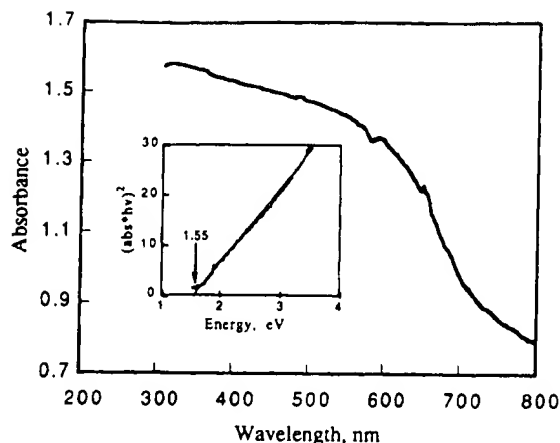
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Attachments: Kamogawa et al. reference (4 pages)  
Sampanthar et al. reference (5 pages)



**Figure 9.** Absorption spectrum of CdSe film as deposited on Ti and removed with Scotch tape. The inset shows a plot of  $(\text{abs} \times h\nu)^2$  vs  $h\nu$  for the same sample.

band edge was not as obvious in all films analyzed, indicating that the electronic properties of this material vary somewhat from sample to sample. Presumably this arises from the very fine grain structure in these films. Deviations from the expected bulk properties of CdSe films have previously been attributed to quantum confinement effects arising from the very small crystallite size obtained with electrodeposited films.<sup>14,17,18</sup> Hot-probe measurement of the as-deposited CdSe films indicated that the material is n-type.

### Conclusions

The cyclic electrodeposition technique used in the present study produces homogeneous films of CdSe that

are close to 1:1 atomic ratio of Cd to Se. The scan parameters are designed to lay down sequential monolayers of CdSe in order to avoid the accumulation of excess Se in the material. For the purpose of producing stoichiometric semiconductor films, this is an improvement over previous potentiostatic or galvanostatic electrochemical techniques, which tend to produce films containing excess Se. The key feature in this process appears to be the continuous deposition and stripping of excess Cd, which is proposed to react with any excess Se that may deposit. The material produced by sequential monolayer electrodeposition contains 3–4% by weight Cl as the major impurity when  $\text{CdCl}_2$  is used as the Cd source. The films produced using the present technique consist of a dense layer underneath scattered dendrites, similar to CdSe films electrodeposited by other routes. In addition, the optical properties of these films are similar to those of previously studied films. Thus, although the present technique provides an improvement in the stoichiometry of electrodeposited films, in other respects the films do not significantly differ from those made by previous routes. Current work is directed at elucidating the mechanism of CdSe growth, characterizing the electronic properties of these films, and extending the procedure to other semiconductor systems.

**Acknowledgment.** We thank Jan Talbot for helpful discussions. A.M.K. thanks the U.S. Department of Education for a graduate fellowship.

**Registry No.** CdSe, 1306-24-7; Ti, 7440-32-6; Ni, 7440-02-0;  $\text{CdCl}_2$ , 10108-64-2;  $\text{CdSO}_4$ , 10124-36-4;  $\text{SeO}_2$ , 7446-08-4;  $\text{H}_2\text{SeO}_3$ , 7783-00-8.

## Redox Photochromism in Films of Viologens and Related Compounds Bearing Long-Chain Alkyl Groups

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1,1'-Bis(benzyl or *p*-methylbenzyl)-4,4'-bipyridinium and *trans*-4,4'-vinylenebis(1-benzylpyridinium) bis-(*p*-alkylbenzenesulfonate)s bearing long-chain alkyl groups (viologen Ia,b), prepared from their respective dichlorides by the anion-exchange reaction, were sandwiched between two glass plates by melting to afford thin transparent and mainly isotropic films. These almost colorless or pale yellow films developed intense visible colors by near-UV irradiation, which bleached upon heating (photochromism). This behavior is considered to be due to reversible redox reactions consisting of the one-electron transfer to viologen Ia,b cation from the counteranion by the photon mode (color development) and vice versa by the heat mode (bleaching).

### Introduction

It has been widely known that some 1,1'-disubstituted bipyridinium, i.e., viologens, and related salts reversibly develop intense colors with visible lifetimes when exposed to radiation of the solar level in solutions in the presence of reductants,<sup>1</sup> in activating matrix polymer films,<sup>2</sup> and in

the crystalline state.<sup>3</sup>

We report here reversible photoreductions accompanied by visible color developments (photochromism), which have been found for thin isotropic films made of the viologens bearing long-chain alkyl groups without any

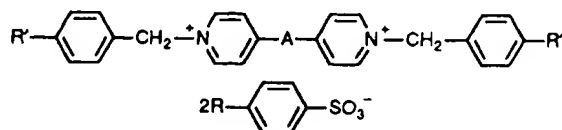
(1) (a) Koizumi, M.; Obata, H. *Bull. Chem. Soc. Jpn.* 1958, 31, 823. (b) Bruin, F.; Heineken, F. W.; Bruin, M.; Zahlen, M. *J. Chem. Phys.* 1962, 36, 2783. (c) Johnson, C. S.; Gutowsky, H. S. *Ibid.* 1963, 39, 58–62. (d) Ledwith, A.; Russel, P. J.; Sutcliffe, L. H. *Chem. Commun.* 1971, 964–965. (e) Ledwith, A. *Acc. Chem. Res.* 1972, 2, 1768–1772. (f) Evans, A. G.; Dodson, N. K.; Raes, N. H. *J. Chem. Soc., Perkin Trans. 2* 1976, 859–863. (g) Takuma, K.; Kajiwara, M.; Matsuo, T. *Chem. Lett.* 1977, 1199–1202. (h) Brown, N. M. D.; Cowley, D. J.; Hashmi, M. *Ibid.* 1978, 462–468. (i) Jones, II, G.; Zisk, M. B. *J. Org. Chem.* 1986, 51, 947–950.

(2) (a) Kamogawa, H.; Masui, T.; Nanasawa, M. *Chem. Lett.* 1980, 1145–1148. (b) Kamogawa, H.; Masui, T.; Amemiya, S. *J. Polym. Sci., Polym. Chem. Ed.* 1984, 22, 383–390. (c) Kamogawa, H.; Sugiyama, M. *Bull. Chem. Soc. Jpn.* 1985, 58, 2443–2444. (d) Kamogawa, H.; Amemiya, S. *J. Polym. Sci., Polym. Chem. Ed.* 1985, 23, 2143–2423. (e) Kamogawa, H.; Satoh, S. *Ibid.* 1988, 26, 653–656. (f) Kamogawa, H.; Nanasawa, M. *Chem. Lett.* 1988, 373–376. (g) Kamogawa, H.; Kikushima, K. *J. Polym. Sci., A: Polym. Chem.* 1989, 27, 393–396.

(3) (a) Kamogawa, H.; Suzuki, T. *J. Chem. Soc., Chem. Commun.* 1985, 525–526. (b) Kamogawa, H.; Suzuki, T. *Bull. Chem. Soc. Jpn.* 1987, 60, 794–796. (c) Kamogawa, H.; Satoh, S. *Ibid.* 1991, 64, 1066–1068.

additives. This has made possible for the first time the color development by light of transparent films based on a redox mechanism consisting of the photon mode color development and the heat mode bleaching.

The compounds prepared and investigated in this study, which are hereafter referred to as "viologens", are shown in Ia,b, where R represents alkyl groups with C<sub>6</sub>–C<sub>15</sub>.



Ia,b: A = none (Ia) or  $-\text{CH}=\text{CH}-$  (Ib); R' = H or CH<sub>3</sub>

## Experimental Section

**Materials.** All reagents employed were of the highest purity and used as received, unless otherwise noted. The alkyl groups (R) of *p*-alkylbenzenes were identified by means of mass spectrometry and gas chromatography.

**Instrumentation.** Infrared (IR), <sup>1</sup>NMR, mass, and EPR spectra were recorded on a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, a Hitachi M808MS spectrometer, and a JES-FE1 XG spectrometer, respectively, under standard conditions. Elemental analyses were made with a Perkin-Elmer 240 instrument. Visible absorption spectra were obtained with a Shimadzu UV-160 spectrophotometer. Gas chromatography was carried out with a Hitachi 164 gas chromatograph fitted with a SE-30 column under a helium stream (30 mL min<sup>-1</sup>).

**1,1'-Dibenzyl-4,4'-bipyridinium Bis(*p*-alkylbenzenesulfonate) (Ia, R' = H).** 1,1'-Dibenzyl-4,4'-bipyridinium dichloride (0.10 g, 0.24 mmol), prepared by refluxing 4,4'-bipyridine with benzyl chloride for 24 h, was dissolved in hot ethanol (50 mL). To the resulting solution was added an anion-exchange resin (Amberlite IRA-900, capacity, 1 mg equiv/mL; 10 mL), loaded with *p*-alkylbenzenesulfonate anion by exchanging the OH<sup>-</sup> type with *p*-alkylbenzenesulfonic acid, which had been synthesized by the sulfonation of *p*-alkylbenzene with 30% fuming sulfuric acid, followed by stirring at 30 °C overnight. The resin was filtered off, and the filtrate was concentrated on a rotary evaporator and precipitated into ether (200 mL) to provide crude product, which was purified by recrystallization from ethanol-ether.

Anal. Calcd for C<sub>28</sub>H<sub>26</sub>N<sub>2</sub>S<sub>2</sub>O<sub>6</sub> (R = *n*-C<sub>6</sub>H<sub>13</sub>): C, 70.24; H, 6.83; N, 3.41%. Found: C, 70.12; H, 6.90; N, 3.31%. Calcd for C<sub>32</sub>H<sub>34</sub>N<sub>2</sub>S<sub>2</sub>O<sub>6</sub> (R = *n*-C<sub>8</sub>H<sub>17</sub>): C, 71.24; H, 7.76; N, 3.19%. Found: C, 71.25; H, 7.83; N, 3.22%. Calcd for C<sub>34</sub>H<sub>38</sub>N<sub>2</sub>S<sub>2</sub>O<sub>6</sub> (R = *n*-C<sub>9</sub>H<sub>19</sub>): C, 71.69; H, 7.52; N, 3.10%. Found: C, 71.60; H, 7.48; N, 3.09%. Calcd for C<sub>36</sub>H<sub>42</sub>N<sub>2</sub>S<sub>2</sub>O<sub>6</sub> (R = *n*-C<sub>10</sub>H<sub>21</sub>): C, 72.11; H, 7.72; N, 3.00%. Found: C, 72.48; H, 7.75; N, 2.86%. Calcd for C<sub>38</sub>H<sub>46</sub>N<sub>2</sub>S<sub>2</sub>O<sub>6</sub> (R = *n*-C<sub>11</sub>H<sub>23</sub>): C, 72.50; H, 7.92; N, 2.92%. Found: C, 72.64; H, 7.97; N, 2.90%. Calcd for C<sub>40</sub>H<sub>50</sub>N<sub>2</sub>S<sub>2</sub>O<sub>6</sub> (R = *n*-C<sub>12</sub>H<sub>25</sub>): C, 72.87; H, 8.10; N, 2.83%. Found: (R = *n*-C<sub>12</sub>H<sub>25</sub>): C, 72.58; H, 8.13; N, 2.90%. (Film no. 11 in Table III): C, 72.84; H, 8.14; N, 2.88%. Calcd for C<sub>42</sub>H<sub>54</sub>N<sub>2</sub>S<sub>2</sub>O<sub>6</sub> (R = *n*-C<sub>13</sub>H<sub>27</sub>): C, 73.23; H, 8.27; N, 2.76%. Found: C, 73.20; H, 8.23; N, 2.76%. Calcd for C<sub>44</sub>H<sub>58</sub>N<sub>2</sub>S<sub>2</sub>O<sub>6</sub> (R = *n*-C<sub>14</sub>H<sub>29</sub>): C, 73.57; H, 8.42; N, 2.68%. Found: C, 73.30; H, 8.37; N, 2.66%. Calcd for C<sub>46</sub>H<sub>62</sub>N<sub>2</sub>S<sub>2</sub>O<sub>6</sub> (R = *n*-C<sub>15</sub>H<sub>31</sub>): C, 73.88; H, 8.58; N, 2.61%. Found: C, 73.45; H, 8.51; N, 2.63%.

IR (KBr) 1190, 1030 ( $-\text{SO}_3^-$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 0.5–2.0 (m, alkyl), 2.5 (t, 4 H, 2CH<sub>2</sub>), 6.0 (s, 4 H, 2CH<sub>2</sub>), 6.9–8.0 (m, 18 H, ArH), 8.8 (d, 4 H, pyridinium), 9.4 (d, 4 H, pyridinium).

**1,1'-Bis(*p*-methylbenzyl)-4,4'-bipyridinium Bis(*p*-dodecylbenzenesulfonate) (Ia, Film No. 12 in Table III).** The same reaction procedure as that for Ia (R' = H) was applied to 1,1'-bis(*p*-methylbenzyl)-4,4'-bipyridinium dichloride to provide a colorless crystalline powder. Anal. Calcd for C<sub>62</sub>H<sub>84</sub>N<sub>2</sub>S<sub>2</sub>O<sub>6</sub>: C, 73.23; H, 8.27; N, 2.76%. Found: C, 73.17; H, 8.30; N, 2.66%. IR (KBr) 1200, 1040 ( $-\text{SO}_3^-$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 0.5–2.0 (m, 46 H, 2C<sub>11</sub>H<sub>23</sub>), 2.3 (s, 6 H, 2CH<sub>3</sub>), 2.5 (t, 4 H, 2CH<sub>2</sub>), 5.9 (4 H, 2CH<sub>2</sub>), 6.9–7.8 (m, 16 H, ArH), 8.8 (d, 4 H, pyridinium), 9.5 (d, 4 H, pyridinium).

***trans*-4,4'-Vinylenebis(1-benzylpyridinium) Bis(*p*-dodecylbenzenesulfonate) (Ib, Film No. 13 in Table III).** This colorless compound was synthesized in the same manner as for

Ia (R' = H), starting with *trans*-4,4'-vinylenebis(1-benzylpyridinium) dichloride, also prepared using *trans*-1,2-bis(4-pyridyl)ethylene instead of 4,4'-bipyridine. Anal. Calcd for C<sub>62</sub>H<sub>82</sub>N<sub>2</sub>S<sub>2</sub>O<sub>6</sub>: C, 73.37; H, 8.09; N, 2.76%. Found: C, 73.25; H, 8.12; N, 2.71%. IR (KBr) 1180, 1040 ( $-\text{SO}_3^-$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 0.5–0.2 (m, 46 H, 2C<sub>11</sub>H<sub>23</sub>), 2.5 (t, 4 H, 2CH<sub>2</sub>), 5.9 (s, 4 H, 2CH<sub>2</sub>), 7.0–7.9 (m, 18 H, ArH), 8.2 (s, 2 H,  $-\text{CH}=\text{CH}-$ ), 8.5 (d, 4 H, pyridinium), 9.3 (d, 4 H, pyridinium).

**Preparation of the Glass-Sandwiched Film.** Finely divided crystals of viologen Ia,b were spread on a glass plate and melted quickly (above 140 °C), followed by the immediate tight covering with another glass plate and cooling to room temperature to afford an almost air-tight glass-sandwiched film ranging in thickness from 0.008 to 0.012 mm. All these operations were carried out in a glovebox filled with purified nitrogen.

The film thus prepared was transparent and almost colorless or pale yellow. The isotropic property of the film was checked with crossed polarizers.

**Light Sources for Photochromic Measurements.** The glass-sandwiched films were subjected to the 10-min irradiation by 366-nm UV light, obtained by passing the light from a 75-W high-pressure mercury lamp (Toshiba SHL-100UV) through a JASCO CT-10S monochromator. A 150-W xenon lamp, fitted with a Toshiba O-59 filter cutting the light below 590 nm, was employed for the visible irradiation on the film, which had been irradiated with the near-UV light and had developed color.

Since the viologens and related compounds described above belong to the same compound group as a herbicide Paraquat,<sup>4</sup> handling in an appropriate manner so as to avoid exposure is recommended.

## Results and Discussion

Viologens Ia,b were synthesized starting with 1,1'-bis(benzyl or *p*-methylbenzyl)-4,4'-bipyridinium dichloride or *trans*-4,4'-vinylenebis(1-benzylpyridinium) dichloride by the anion-exchange reaction using an anion-exchange resin.

Fine powders of the viologens thus synthesized were heated just to their melting points (>140 °C) under nitrogen and then sandwiched between two glass plates to provide air-tight thin films free of oxygen. The glass-sandwiched films thus prepared, which were transparent and mainly isotropic, were subjected to near-UV irradiation (366 nm) from a 75-W high-pressure mercury lamp for 10 min, and the resulting absorbance increases in the visible region were recorded.

With the irradiation, initially colorless or pale yellow films gradually developed visible colors with almost linear increases of absorbances.

Figure 1 indicates typical absorption spectra obtained when the irradiation was stopped after 10 min.

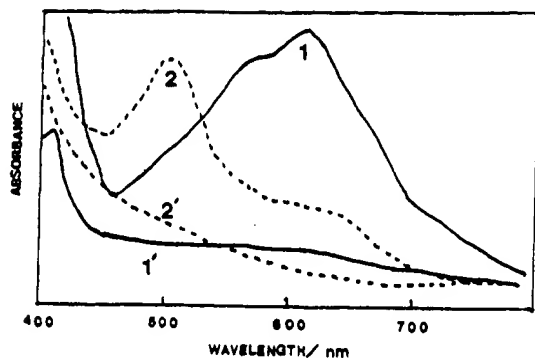
It is recognized in this figure that absorption spectra based on the transmission of light, the measurements of which had been impossible for viologen crystals,<sup>3</sup> could be determined satisfactorily.

The shape and position of absorption maximum (ca. 600 nm, blue coloration) of curve 1 are quite similar to those of the radical cations derived from the conventional viologens in solutions<sup>5</sup> and viologen crystals,<sup>3</sup> and those of curve 2 are also consistent with the characteristics of the absorption spectra including a lot of the associated radical cations.<sup>6</sup> Moreover, EPR spectra exemplified in Figure 2 correspond exactly to the absorption change, so that it is confirmed that the radical cation was produced by the one-electron transfer from the counteranion to viologen dication, as demonstrated in the case of viologen crystals.<sup>3</sup> However, no appreciable differences in the IR

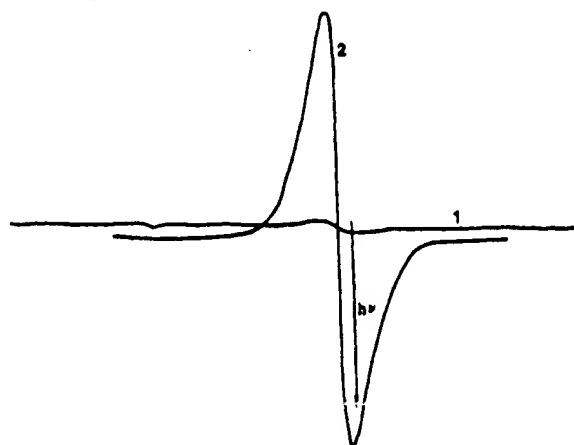
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(5) Bockman, T. M.; Kochi, J. K. *J. Org. Chem.* 1990, 55, 4127–4135.

(6) Yamana, M.; Kawada, R. *Nippon Kagaku Kaishi* 1977, 7, 941–946.



**Figure 1.** Typical visible absorption spectra for the glass-sandwiched viologen Ia,b films subjected to near-UV irradiation. Curves 1 and 1' indicate the spectrum immediately after irradiation and that before irradiation or upon a 10 min standing at 70 °C after irradiation, respectively, in the case of R = 70% *n*- + 30% highly branched C<sub>12</sub>H<sub>25</sub> and R' = H (Ia); curves 2 and 2' are those in R = *n*-C<sub>14</sub>H<sub>29</sub>. The measure of absorbance is arbitrary only to show the shapes of absorption spectra.

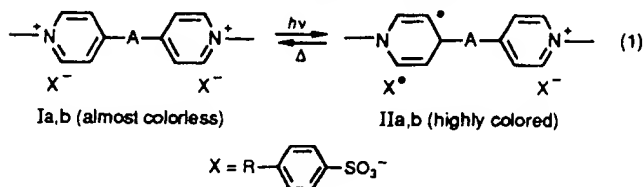


**Figure 2.** Typical EPR spectra for the glass-sandwiched viologen Ia,b films subjected to near-UV irradiation. Spectra 1 and 2 correspond to 1' and 1 in Figure 1, respectively. Measurement conditions: field, 3290 G + 250 G; modulation 100 kHz; amplitude, 1.25 × 10; response, 0.01.

spectrum were recognized between before and after irradiation, presumably because the change in concentration is so small as to not be detectable.

Figure 1 also indicates that these increases in visible absorption induced by light can be recovered to the original states 1' and 2' upon 10 min of standing at 70 °C.

Such being the case, the reversible relation given in eq 1 may exist between the original viologen Ia,b and the



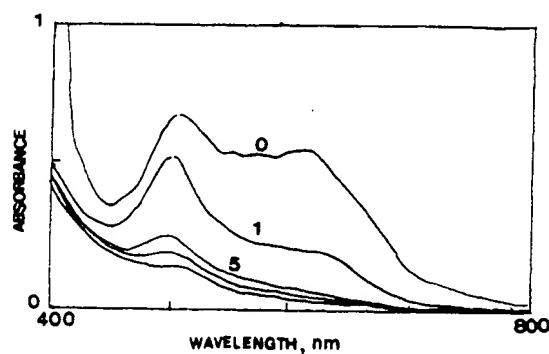
radical ion pair IIa,b produced as a result of irradiation. Namely, as for viologens Ia,b bearing long alkyl chains, reversible photoredox reactions, i.e., intense color development by the photon mode and bleaching of the developed color by the heat mode (redox photochromism), may take place in the absence of oxygen.

A typical example indicating the effect of temperature on bleaching of the color developed by light is given in Table I. It is recognized in this table that the initial bleaching rate ( $A/A_0$ ) at  $\lambda_{\text{max}}$  increased rapidly with temperature, and in this case bleaching was almost complete

**Table I.** Effect of Temperature on Bleaching of the Color Developed in a Typical Viologen Film<sup>a</sup> by Near-UV Light

expt. no.	temp, °C	init bleaching rate <sup>b</sup> $A/A_0$ (613 nm), min <sup>-1</sup>
1	30	0.03
2	40	0.24
3	50	0.66
4	60	0.72
5	70	0.99
6	80	1.00
7	90	1.48
8	70	2.10 <sup>c</sup>
9	70	0.12 <sup>d</sup>
10	Xe lamp <sup>e</sup>	0.01

<sup>a</sup> Viologen corresponding to curves 1 and 1' in Figure 1 [R = 70% *n*- + 30% highly branched C<sub>12</sub>H<sub>25</sub>; R' = H (Ia)]. <sup>b</sup>  $A_0$ : absorbance increase at 613.0 nm induced by light. A: Initial decrease of absorbance reduced to 1 min. <sup>c</sup> In the presence of a half-molar excess of *p*-dodecylbenzenesulfonic acid. <sup>d</sup> Viologen anions are composed of RPhSO<sub>3</sub><sup>-</sup>Cl<sup>-</sup> in 3:1 molar ratio. <sup>e</sup> 150 W, >590 nm, 5 cm × 1 h.



**Figure 3.** Typical change of the visible absorption spectra developed for viologen Ia,b films by light with heating at 70 °C. Absorption spectra are those for viologen Ia with R = 70% *n*- + 30% highly branched C<sub>12</sub>H<sub>25</sub> and R' = CH<sub>3</sub>. Figures in the diagram denote standing times at 70 °C in minutes after irradiation.

at 70 °C in 1 min (expt no. 5). Irradiation of visible light above 590 nm on the colored film, however, provided little changes (expt no. 10), thereby suggesting that the back reaction was of the heat mode nature. It can be also seen in Table I that the presence of excess *p*-dodecylbenzenesulfonic acid in the film enhanced the bleaching rate significantly (expt no. 8), presumably due at least partly to a plasticizing effect; lack of RPhSO<sub>3</sub><sup>-</sup> caused the reverse effect (expt no. 9), as expected.

It is also recognized in Figure 3 that the absorbance peak around 600 nm attributable to the monomeric radical cation, as mentioned above, decreases more rapidly by heating than the peak around 500 nm attributable to the associated ones does, indicating that the former is less stable thermally than the latter. This is a general tendency in the present study.

Effects of the kind of viologen Ia,b on the visible absorption changes induced by light, i.e., photochromic behavior by redox mechanism, as determined by transmittance, are summarized in Tables II and III.

It is known from Table II that both isotropic properties and photoredox behavior of the film are affected significantly by the chain length of R. Thus, as for Ia with R composed of an *n*-alkyl group alone, the values of the absorbance increase induced by UV irradiation were reduced to those for the 0.01-mm film thickness in order to prevent errors caused by slight deviations from 0.01-mm thickness. The corrected absorbance increase, i.e., photosensitivity, at  $\lambda_{\text{max}}$  around 500 nm appears to first become larger with an increase in carbon number to reach

Table II. Effect of Chain Length of R on Photochromic Behavior of Viologen Ia (R' = H) Films<sup>a</sup>

film no.	R	abs increase <sup>b</sup> induced by light		A/A <sub>0</sub> , <sup>c</sup> min <sup>-1</sup>	isotropic <sup>d</sup> property of film
		ca. 500 nm	610 nm		
1	<i>n</i> -C <sub>9</sub> H <sub>13</sub>	0.362 (504) <sup>e</sup>	0.190	0.36	transparent but a little anisotropic
2	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	0.625 (505) <sup>e</sup>	0.318	0.45	transparent but a little anisotropic
3	<i>n</i> -C <sub>9</sub> H <sub>19</sub>	0.788 (506) <sup>e</sup>	0.421	0.48	transparent and isotropic
4	<i>n</i> -C <sub>10</sub> H <sub>21</sub>	0.787 (506) <sup>e</sup>	0.451	0.52	transparent and isotropic
5	<i>n</i> -C <sub>11</sub> H <sub>23</sub>	0.783 (507) <sup>e</sup>	0.441	0.46	transparent and isotropic
6	<i>n</i> -C <sub>12</sub> H <sub>25</sub>	0.690 (506) <sup>e</sup> 0.686 (506) <sup>f</sup>	0.379	0.43	transparent and isotropic
7	<i>n</i> -C <sub>13</sub> H <sub>27</sub>	0.571 (505) <sup>e</sup>	0.279	0.41	transparent and isotropic
8	<i>n</i> -C <sub>14</sub> H <sub>29</sub>	0.469 (505) <sup>e</sup>	0.200	0.41	transparent but a little anisotropic
9	<i>n</i> -C <sub>15</sub> H <sub>31</sub>	0.360 (505) <sup>e</sup>	0.179	0.37	transparent but a little anisotropic

<sup>a</sup> See Experimental Section. <sup>b</sup> Reduced to 0.01-mm film thickness. <sup>c</sup> See Table I. Values at λ<sub>max</sub> around 500 nm. <sup>d</sup> Determined with crossed polarizers. <sup>e</sup> Values at λ<sub>max</sub> indicated in parentheses. <sup>f</sup> Values after 50 cycles of irradiation and subsequent thermal bleaching (70 °C × 10 min).

Table III. Effect of R, R', and A in Viologens Ia,b on Color Development by Light<sup>a</sup>

film no.	R	R'	A	abs increase <sup>b</sup> induced by light		isotropic <sup>c</sup> property of film
				ca. 500 nm	610 nm	
10	mixture <sup>e</sup>	H	none	0.612 (507) <sup>d</sup>	0.522 <sup>f</sup>	transparent and isotropic
11	C <sub>12</sub> H <sub>25</sub> <sup>g</sup>	H	none	0.242 (500)	0.793 (613) <sup>d</sup> 0.791 (613) <sup>h</sup>	transparent and isotropic
12	C <sub>12</sub> H <sub>25</sub> <sup>g</sup>	CH <sub>3</sub>	none	0.672 (509) <sup>d</sup>	0.549 (612) <sup>d</sup>	transparent and isotropic
13	C <sub>12</sub> H <sub>25</sub> <sup>g</sup>	H	—CH=CH—	0.322 (535) <sup>d</sup>	0.107 <sup>f</sup>	transparent and isotropic

<sup>a</sup> See Experimental Section. <sup>b-d</sup> See Table II. <sup>e</sup> Mixture of viologens with R = *n*-C<sub>8</sub>H<sub>17</sub>, *n*-C<sub>10</sub>H<sub>21</sub>, *n*-C<sub>12</sub>H<sub>25</sub>, and *n*-C<sub>14</sub>H<sub>29</sub> in an equimolar quantity. <sup>f</sup> Shoulder. <sup>g</sup> 70% *n*- + 30% highly branched. <sup>h</sup> Values after 50 cycles of irradiation and subsequent thermal bleaching (70 °C × 10 min).

a maximum at C<sub>9-11</sub> and then become gradually smaller with a further increase in carbon number. The value of the λ<sub>max</sub> and the isotropic property of the film determined with crossed polarizers, which is considered to stand for amorphous character, varied corresponding to the photosensitivity change.

It can be concluded from these results that, within the scope of the present experimental conditions, the isotropic property of film Ia is gradually improved with an increase in carbon number to reach the best amorphous character at C<sub>9-11</sub>, causing the highest photosensitivity. The amorphous character becomes worse, however, with a further increase in carbon number, presumably due to the crystallization effect of the long alkyl chains among each other.

It is also known from Table II that better isotropic films may afford larger values of A/A<sub>0</sub>, consisting with the results in Table I.

The results summarized in Tables II and III differ from those obtained for viologen crystals, previously reported,<sup>3a,b</sup> particularly in that this kind of photochromism was observed for all viologen films investigated and associations of radical cations were much more marked especially in the case of R = *n*-C<sub>n</sub>H<sub>2n+1</sub> (Table II), indicating that the dicationic and counteranionic parts of the viologen molecule are situated next to each other at the sites permitting the general occurrence of the light-induced reaction shown in eq 1 and that the dications tend to lie at the sites, where

the association of the radical cations produced therefrom could take place.

Mixing anions bearing varied R, which may also cause a plasticizing effects, is favorable in that it affords an isotropic film, in which the monomeric radical cation (λ<sub>max</sub>, ca. 600 nm) may exist in a high content, and that a high photosensitivity is obtained (see curve 1 in Figure 1 and film nos. 10–12 in Table III).

Viologen Ib bearing the conjugated —CH=CH— group provided similar results. A typical example is given also in Table III (film no. 13).

In this case, however, the absorption peak around 400 nm found for the radical cation from Ia, as seen in Figures 1 and 3, appears to be red-shifted to 535 nm (red coloration) through extended conjugation.

As can be supposed from Tables II and III (expt nos. 6 and 11), viologen films of the present study could be subjected to at least 50 photochromic redox cycles, one of which was composed of the irradiation as described in the Experimental Section and subsequent 10 min standing at 70 °C.

**Registry No.** 1a (R' = H)(R = *n*-C<sub>8</sub>H<sub>13</sub>), 136893-34-0; 1a (R' = H)(R = *n*-C<sub>8</sub>H<sub>17</sub>), 136893-35-1; 1a (R' = H)(R = *n*-C<sub>9</sub>H<sub>19</sub>), 136893-36-2; 1a (R' = H)(R = *n*-C<sub>10</sub>H<sub>21</sub>), 136893-37-3; 1a (R' = H)(R = *n*-C<sub>11</sub>H<sub>23</sub>), 136893-38-4; 1a (R' = H)(R = *n*-C<sub>13</sub>H<sub>27</sub>), 136893-40-8; 1a (R' = H)(R = *n*-C<sub>14</sub>H<sub>29</sub>), 136893-42-0; 1a (R' = H)(R = *n*-C<sub>15</sub>H<sub>31</sub>), 136893-44-2; 1a (R' = Me)(R = *n*-C<sub>12</sub>H<sub>25</sub>), 136893-45-3; (E)-1b (R' = H)(R = *n*-C<sub>12</sub>H<sub>25</sub>), 136893-47-5.

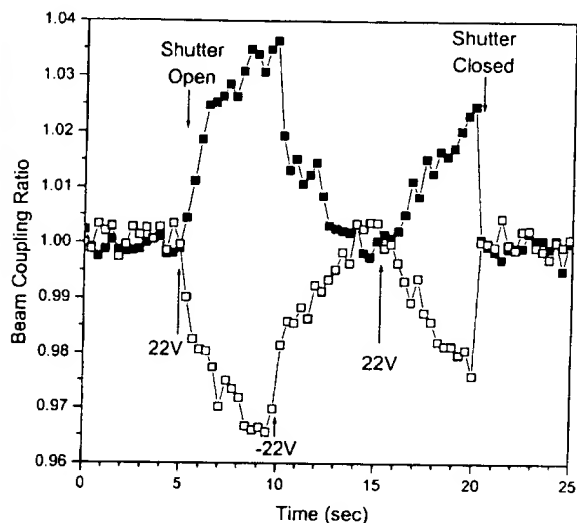


Fig. 4. The change of the beam coupling ratio when the applied voltage is switched from 22 V to -22 V is shown. The rapid initial decrease is due to the reorientation of the FLC director to a less optimal orientation for photorefractivity. The slower change is due to the erasure of the space-charge field.

as charges begin to redistribute in response to the applied field polarity change. At 20 s, the voltage is switched back to 22 V, and the initial charge modulation begins to reform.

We have observed for the first time orientational photorefractivity in FLC composites containing easily oxidized and reduced chromophores. The applied field dependence suggests that the orientational response is a result of the space-charge field coupling to the bulk polarization of the FLC and not to dielectric anisotropy as with nematic liquid crystals. In order to increase the likelihood of observing the linear electro-optic effect in addition to orientational contributions, one possibility is to use homeotropically aligned FLCs with a transverse applied field, so that the modulated space-charge field lies along the polar axis of the FLC. The use of FLCs specifically designed to increase  $P_s$  and the electronic electro-optic effect would also prove advantageous for improving the performance of these novel materials.

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## Flexible Smart Window via Surface Graft Copolymerization of Viologen on Polyethylene

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Sock Wee Ng, En Tang Kang, and Kuang Lee Tan

The development of chromogenic materials for glazing "smart" or "intelligent" windows has been actively pursued in recent years. The change in the optical properties of these materials may be activated by electricity, heat, or light. Examples of commonly used chromogenic materials are certain transition-metal oxides such as  $\text{WO}_3$ ,  $\text{NiO}$ ,  $\text{MoO}_3$ , and organic compounds such as viologens, dipthalocyanines, and polyaniline.<sup>[1-5]</sup> The viologens are among the most studied chromogenic materials and the change in coloration is achieved by an oxidation-reduction reaction. However, since the short-chain viologens are soluble in water, various methods of synthesizing viologen-containing chromogenic systems have been developed. These include the incorporation of viologens into anionic polyelectrolyte films,<sup>[6]</sup> iminodiacetic acid-type chelate resin beads,<sup>[7]</sup> and *N*-vinyl-2-pyrrolidone-methyl acrylate copolymers,<sup>[8]</sup> as well as the casting of ruthenium(II) complex and viologen containing partially quarternized poly(1-vinylimidazole) into films.<sup>[9]</sup>

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Our group and others have carried out surface modification of polymeric substrates via graft copolymerization to impart new and specific functionalities to the polymer surface.<sup>[10-14]</sup> In this paper, we report on the use of this strategy to incorporate a thin layer of viologen polymer on the surface of low-density polyethylene (LDPE) film. This viologen-LDPE system serves as a transparent "smart" window whose transmittance is reduced when exposed to light. This type of system offers the advantage of being a thin flexible film that can be shaped and is suitable for large area displays. Furthermore, the thin surface layer of viologen polymer offers a rapid photochromic response.

The method we employed to covalently bond the viologen moieties onto the surface of the LDPE film involves first the UV-induced graft copolymerization of 4-vinyl benzyl chloride on the plasma-pretreated LDPE film surface. The pendent benzyl chloride groups of the grafted 4-vinyl benzyl chloride polymer chain on LDPE film surface then serve as functional groups for the introduction of the viologen moiety onto the LDPE surface via reaction with 4,4'-bipyridine followed by benzyl chloride or other alkyl halides. The reaction route is given in Scheme 1. The proportion of the 4-vinyl benzyl chloride successfully reacted with 4,4'-bipyridine is represented by "y" in Scheme 1. The amount of viologen on the film surface can be varied by varying the amount of vinyl benzyl chloride grafted on the film surface (Step 1 in Scheme 1) and the type of alkyl halides (e.g., benzyl chloride) used in the subsequent reaction (Step 3 in Scheme 1). The graft concentration of the vinyl benzyl chloride in turn depends on the monomer concentration, the plasma treatment time, and the UV-induced reaction time. Table 1 shows how the plasma treatment time

Table 1. Surface graft concentration of 4-VBzCl copolymer as a function of argon plasma treatment time and UV-induced reaction time.

Sample no.	Argon plasma treatment time [s]	UV-induced reaction time [min]	Graft concentration [a]
1	60	15	0.14
2	60	20	0.22
3	60	30	0.40
4	60	60	0.48
5	60	120	0.27
6	90	15	0.05
7	90	20	0.05
8	90	30	0.06
9	90	45	0.24
10	90	60	0.44
11	90	120	0.19

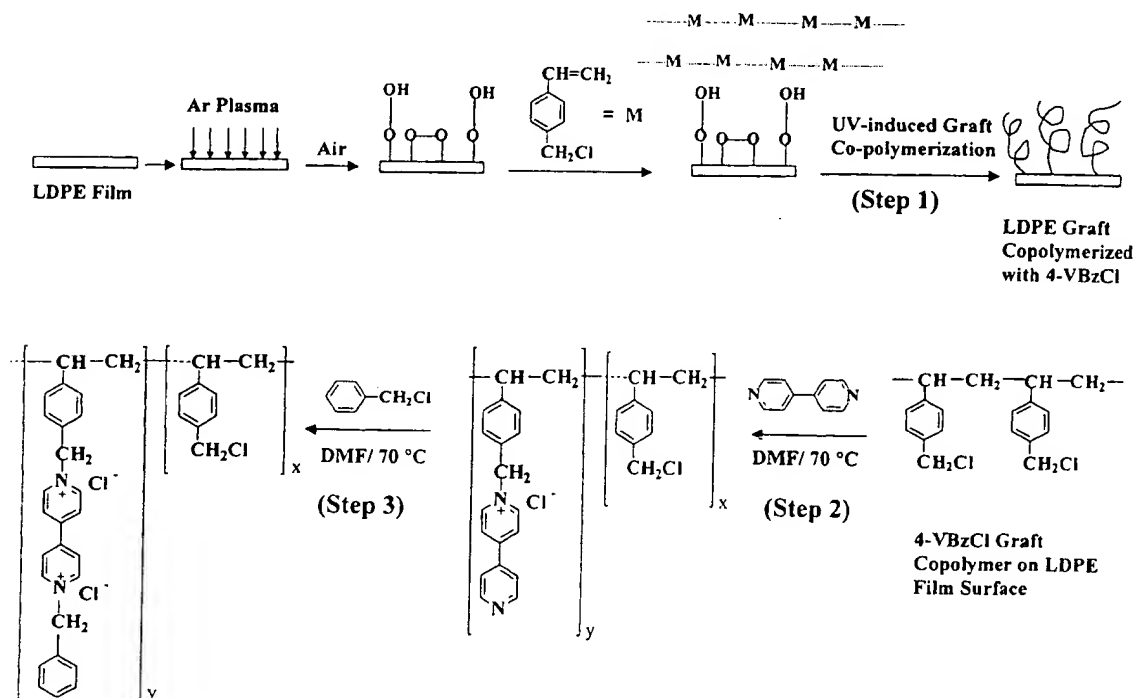
[a] Obtained from XPS measurement using the following equation:

$$\frac{M_{VBzCl}}{M_{ethylene}} = \frac{\text{peak area of Cl 2p}}{[\{\text{peak area of total C 1s}\} - \{\{\text{peak area of Cl 2p}\} \times 9\}]/2} \quad (1)$$

where the peak area has been corrected with the appropriate sensitivity factor, and the factors of 9 and 2 account for the nine carbon atoms associated with each 4-VBzCl unit and the two carbons per repeating ethylene unit, respectively.

and the UV-irradiation time affect the graft concentration of vinyl benzyl chloride (defined as number of vinyl benzyl chloride units per repeating ethylene unit of LDPE).

The viologen grafted LDPE films were characterized by UV-vis absorption spectroscopy and X-ray photoelectron spectroscopy (XPS) measurements. The UV-vis absorption spectrum of the film (labeled "before irradiation" in Fig. 1) shows an absorption band below 380 nm attributable to the viologen dication (denoted as BV<sup>2+</sup> for benzyl viologen).<sup>[15]</sup> During the XPS measurements, the color of the film in the XPS chamber was observed to change from very faint yellow to blue. The color change is due to the reduction of the BV<sup>2+</sup>



Scheme 1. Reaction route used to synthesize the viologen grafted LDPE films.

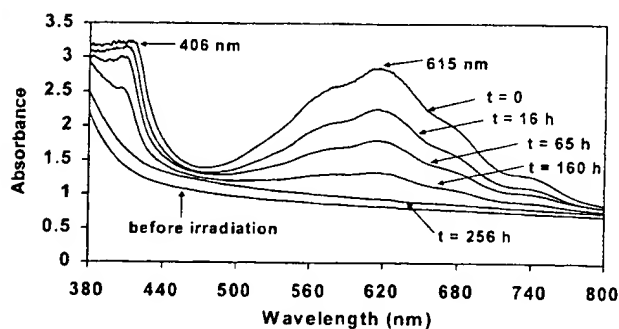


Fig. 1. UV-vis absorption spectra of viologen grafted LDPE film before and after 3 min irradiation and during bleaching under vacuum. (Time indicated denotes the time after irradiation has stopped.)

to the monocation radicals ( $BV^{+\bullet}$ ) under X-ray irradiation and has also been reported earlier.<sup>[16]</sup> The XPS N 1s core level spectrum of the viologen grafted LDPE film shows two well resolved peaks due to nitrogen radical ( $N^{\bullet}$ ) at 399.6 eV and positively charged nitrogen ( $N^+$ ) at 401.8 eV (as illustrated in Figure 2a for Sample 10). There is no peak due to the neutral nitrogen atom ( $-N=$ ), which suggests that Step 3 is efficient at

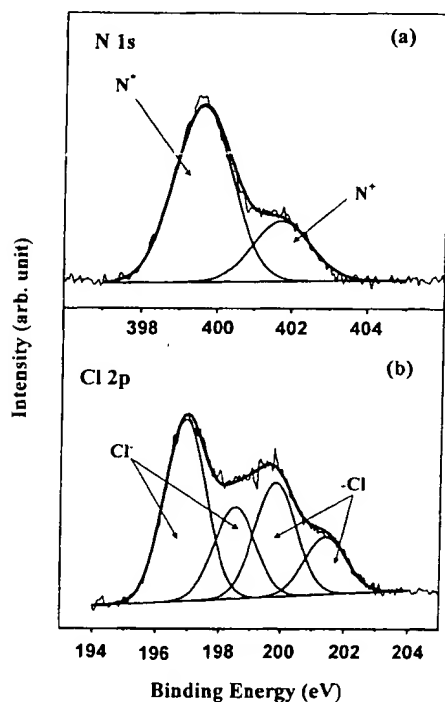
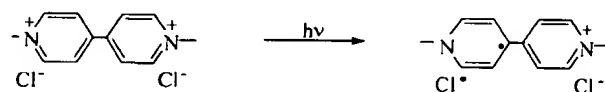


Fig. 2. XPS a) N 1s and b) Cl 2p core level spectra of a viologen grafted LDPE film (Sample 10).

converting both N atoms of the bipyridyl ring to the diquaternized nitrogen cation ( $N^+$ ). The Cl 2p core level spectrum shows component peaks due to chloride anions,  $Cl^-$ , and covalently bonded chloride,  $-Cl$  (Fig. 2b). The presence of the latter indicates that some benzyl chloride groups in the 4-vinyl benzyl chloride graft copolymer did not react with the 4,4'-bipyridine (proportion represented by "x" in Scheme 1). This may be due to steric hindrance between the benzyl rings, which inhibits the reaction of the 4,4'-bipyridine with every

benzyl chloride group. The  $Cl^-/N^+$  ratio of the viologen grafted films is readily calculated from the deconvoluted XPS N 1s and Cl 2p spectra. The  $Cl^-/N^+$  ratio calculated for the viologen grafted LDPE films with vinyl benzyl chloride graft concentration ranging from 0.05 to 0.44 is between 0.82 and 1.04. This confirms that charge neutrality is maintained. Hence, the UV-vis absorption spectroscopy and XPS measurements confirm the presence of viologen moieties that are covalently bonded to the LDPE surface even after extensive washing with organic solvents (please refer to the Experimental section).

A number of applications can be envisaged for polymeric substrates with surface graft copolymerized viologen moieties. When the viologen grafted LDPE films are exposed to near-UV irradiation for 1 to 3 min at room temperature, the color of the film changes from faint yellow to blue. As mentioned earlier, this color change results from the conversion of the viologen dication to the monocations<sup>[15]</sup> and may be represented by Scheme 2.<sup>[8,17]</sup>



Scheme 2. Photoinduced conversion of viologen dication to monocation.

When the irradiation is stopped, the reverse reaction  $BV^{+\bullet} \rightarrow BV^{2+}$  occurs. These color changes occur very rapidly in air. To illustrate these color changes, experiments to record the UV-vis absorption spectra of the film were carried out with the film in a vacuum tube. Figure 1 shows the UV-vis spectrum of the Sample 3 film immediately after irradiation by a high-pressure 1 kW Hg lamp placed 4 cm from the film ( $t = 0$  curve) and the spectra as the film bleaches with time under vacuum. The shape and position of absorption maximum ( $\lambda_{max}$ ) of the  $t = 0$  curve is quite similar to those reported earlier for radical cations derived from the viologens in solution,<sup>[18]</sup> or in the form of crystals<sup>[19]</sup> or films.<sup>[17,20]</sup> The viologen monocation radical ( $BV^{+\bullet}$ ), which is the one-electron reduced form of viologen dication, gives rise to  $\lambda_{max}$  at about 615 nm and 406 nm, while that of its associated species or the dimeric form ( $BV_2^{2+}$ ) is at about 560 nm.<sup>[15,17,21]</sup> The response of the viologen grafted film to several cycles of irradiation and bleaching is shown in Figure 3. These experiments were carried out with a filter, which reduces the intensity of the 1 kW Hg lamp by 50 % and cuts off the irradiation below 350 nm. From Figure 3, it can be seen that the response of the film is very rapid in air (compared to Fig. 1, which shows the slow bleaching in vacuum). This film exhibits a high degree of stability and after 8 cycles, the maximum absorbance at 615 nm does not change significantly ( $<1\%$ ). The response time curve during bleaching also remains essentially unchanged.

In conclusion, we have demonstrated a technique whereby a thin layer of viologen can be incorporated via surface graft copolymerization with a polymeric substrate. The latter lends mechanical strength and flexibility while the thin viologen layer minimizes the amount of viologen required and offers a rapid and reproducible response to UV-vis irradiation. Work

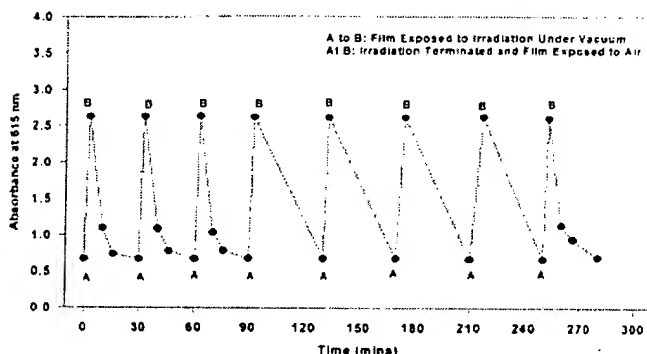


Fig. 3. Response of viologen grafted LDPE film (Sample 3) subjected to cyclic irradiation. (For cycles 1–3 and 8, the absorbance at 615 nm was monitored 7, 13, and 30 min after termination of irradiation. For cycles 4–7, the absorbance was measured 40 min after termination of irradiation.)

is in progress on extending this technique to complexes of viologen with other chromogenic materials and on tailoring these complexes to specific applications.

## Experimental

**Materials and Reagents:** 4-vinyl benzyl chloride (4-VBzCl) (monomer) used for graft copolymerization was obtained from Sigma Aldrich at a purity of 90 % (other isomers account for the remaining 10 %) and was used as received. Benzyl chloride was obtained from BDH (purity 98.5 %) and used without further purification. 4,4'-Bipyridine was obtained from Sigma Aldrich and used as received. The solvents and other reagents were of reagent grade and were used without further purification. LDPE film (of thickness 0.125 mm) was obtained from Goodfellow Corporation, UK.

**Material Characterization:** The UV-vis absorption spectra were recorded on a Shimadzu Model UV-3101PC. The XPS measurements were made on an AXIS HSI-165 ULTRA spectrometer (Kratos Analytical Ltd, England) with a Mg K $\alpha$  X-ray source (1253.6 eV photons). The details of the experiment are given in previous publications [13,22].

**Viologen Grafting on LDPE Film:** LDPE films were cut into 2 cm  $\times$  5 cm pieces, washed with acetone (using an ultrasonic bath for 1 h), and then dried under vacuum for 1 h. The cleaned LDPE films were treated with Ar plasma for either 60 s or 90 s on each side in an Anatech SP100 plasma system, equipped with a cylindrical quartz reactor chamber. The glow discharge was produced at a plasma power of 35 W, an applied frequency of 40 kHz, and an argon pressure of 0.6 torr. The plasma-treated films were exposed to the atmosphere for about 5 min to facilitate the formation of surface peroxides and hydroperoxides, which would initiate the subsequent graft copolymerization of 4-vinyl benzyl chloride monomer. A drop of 4-vinyl benzyl chloride (approximately 50  $\mu$ L) was spread on both sides of the Ar plasma-pretreated film, which was then tightly clipped between two quartz plates and placed in a UV photochemical reactor (Riko Rotary, Model RH 400-10W) for a predetermined period of time (from 10 min to 2 h) at 25  $^{\circ}$ C. After UV irradiation, the film was removed from the plates (after a few hours of soaking in ethanol or DMF solution).

The LDPE film after reaction with vinyl benzyl chloride was washed with dimethylformamide (DMF) for a few hours to remove the residual monomer and homopolymer from the film. After washing, the film was dried under vacuum for 2 h before reacting with 10 % w/v 4,4'-bipyridine in DMF solution (30 mL). The reaction mixture was heated in a water bath at 70  $^{\circ}$ C for 10 h. The films were then removed from the solution, washed with DMF and acetone, and further treated with benzyl chloride in DMF (30 mL) for another 10 h at 70  $^{\circ}$ C. The films were taken out, washed thoroughly with DMF and ethanol, and then dried under vacuum for 1 h. Since the viologen grafted films are sensitive to light, these films were stored in the dark before they were subjected to further testing.

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## Electron Transport in Fluorinated Copper-Phthalocyanine

By Jan H. Schön,\* Christian Kloc, Zhenan Bao, and Bertram Batlogg

Transistor circuits based on organic transistors have been proposed for a variety of applications such as large-area electro-optic displays or identification tags.<sup>[1–3]</sup> For digital circuits the advantages of complementary logic include low power dissipation, robust operation, and ease of circuit design. However, only a few organic semiconductors have proven high performance and stability in air for n-channel operation.<sup>[4–6]</sup> One of these promising materials is copper hexadecafluorophthalocyanine (F<sub>16</sub>CuPc). Thin-film field-effect transistors (FETs) with mobilities exceeding 10<sup>–2</sup> cm<sup>2</sup>/V s have been demonstrated.<sup>[4]</sup> In addition, large-scale integration and fast complementary logic circuits have been reported.<sup>[7,8]</sup> In order to improve device performance and understand the intrinsic charge transport mechanism, we studied the electrical properties of F<sub>16</sub>CuPc single crystals in air as functions of time and temperature. Furthermore, we investigated the mobility in thin-film devices as functions of gate bias and temperature.

Single crystals of F<sub>16</sub>CuPc have been grown from the vapor phase in a stream of gas using a similar technique as for other organic semiconductor materials.<sup>[9]</sup> Needle-like single crystals of several mm length and several 100  $\mu$ m width were obtained. The charge-transport properties in the direction parallel to the long axis (*b*-axis) of the samples with thermally evaporated

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